# XENOBIOTIC ORGANIC COMPOUND CYCLING IN COASTAL WATERS

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## LONG TERM GOALS

Our long term goal is to develop the basis to predict the fates of xenobiotic organic chemicals in harbors and coastal marine environments. To this end, we seek to build a flexible modeling approach that is capable of yielding estimates of chemical concentrations in space and time, tunable for various compounds and coastal environments of interest. Such predictions are necessary to allow us to manage wisely our coastal discharges and to evaluate the need to cleanup existing conditions.

## OBJECTIVES

In order to assess organic chemicals in coastal marine environments, we must (1) be able to characterize the processes controlling their chemical speciation. and (2) be able to evaluate the rates of processes affecting particles in coastal seawater. The first objective requires us to examine the distribution of contaminants like PCBs and PAHs among dissolved, colloidal, and settling particle phases. Moreover, we seek to find properties of the sorbates, sorbents, and solutions from which these "phase" distributions can be estimated a priori. The second objective requires us to assess quantitatively the fluxes of solids from the water column to the sediment beds below.

## APPROACH

Our approaches for examining the phase distributions of organic contaminants in coastal seawaters has involved two aspects in the last year. First, we have used time-resolved fluorescence quenching and small concentrations of spiked fluorophores to observe the importance of colloidal phases for binding such organic chemicals. Additionally, we have worked to measure the presence of a very special sorbent medium, soot, which appears to play a very significant role in the speciation of combustion-derived pollutants like PAHs.

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Our approaches for examining the settling of particles have involved using both water-column and sediment-bed measurements. First, by measuring U238-Th234 disequilibria in the water column, we have extracted a settling rate constant for the suspended solids at any particular site and time. Application of this rate coefficient, along with particulate concentrations of organic compounds, enables us to calculate the export fluxes of those organic chemical from the water column. Our second approach to verify these water column deductions involves use of Pb210-dated sediment cores to
evaluate the import fluxes of the same chemicals into the bed. Comparisons of these two independent measures is used to demonstrate the effectiveness of the U238-Th234 disequilibrium approach.

## WORK COMPLETED

We completed our efforts to devise a method to quantify the dilute sedimentary soot phase (ES&T, 31, 203, 1997.) Non-soot organic carbon is removed by thermal oxidation, and inorganic carbonates are removed by acidification. Subsequent CHN elemental analysis yields a measure of any soot. The selectivity of the method was confirmed in tests with matrices of known composition. The technique was also applied to two sets of natural sediments, both previously analyzed for PAHs.

The importance of soot as a PAH sorbent was examined indirectly (ACS Symposium Series #671, 365, 1997.) First, the concentrations of PAHs in several cores was compared to the soot contents of those same cores. Moreover, estimates were made from the soot-water partition coefficients for PAHs and these were assessed for the likelihood that soot-sorption is a quantitatively important phenomenon for PAHs in coastal marine environments.

The importance of colloid associations was assessed for hydrophobic organic compounds in seawaters obtained along a transect from Portland Harbor out into the Gulf of Maine (Wilkinson Basin). Time-resolved and fluorescence quenching data for probe PAHs added to these seawaters revealed the limited effect of the natural colloids on the PAH speciation. We also prepared a mini-review concerning the current challenges of working on colloids in natural waters (Limnol. Oceanogr. 42, 519, 1997.)

We also used our data to examine the importance of combustion-derived carbon particle sequestration in accumulating coastal sediments (Geochim. Cosmochi. Acta, in press.) This was done by combining our sediment core radiochronology information with our direct measures of soot in those same cores.

Finally, we have also examined the export fluxes of PAHs (Marine Chem. 57, 11, 1997) and PCBs (Environ. Sci. Technol., in press) out of coastal surface waters. We were able to demonstrate that water column export compared favorably with core accumulations of the same compounds. Areal integration of the fluxes allowed us to ascertain the likely important of these fluxes to the overall fates of these organic pollutants.

## RESULTS

First, we now have strong evidence for the importance of soot particles in controlling the speciation of PAHs in coastal environments. Such soot appears to maintain unexpectedly low dissolved PAH concentrations in waters and sediments where the total (dissolved plus particulate) PAH levels are quite high. Additionally, we have deduced that the soot carbon contributes about 10% of the total carbon buried in coastal sediments off New England.

Also, we have found that fluxes of PAHs and PCBs from the water column to the sediments below are a very important of those compounds' cycling. Fluxes of PAHs are seen to decrease exponentially with distance from shore. For individual PAHs like pyrene, aerially integrated fluxes indicate that as much as 60 metric tons per year of this compound are being removed to depth in the North Atlantic; only 10% of this mass is being deposited close to shore. For PCBs we found that the more highly chlorinated compounds exhibited a faster fall off in their fluxes as a function of offshore distance, implying that particle scavenging phenomena (rather that hydroxyl radical degradation) are serving as the chief mechanisms affecting the cycling of these organic contaminants. Again, individual PCB congeners like (#52) tetrachlorobiphenyl are being deposited from into the North Atlantic at rates like 4 metric tons per year, with only 5% within about 20 km of the coast.

## IMPACT

Our finding that the very important class of organic pollutants, the PAHs, are substantially soot-bound in coastal environments has major implications concerning assessments of their toxicity and susceptibility to biodegradation cleanup. Since current efforts to establish sediment quality criteria for such organic compounds are based on the assumption that the solid-water partitioning of PAHs involves only the uptake into amorphous natural organic matter, use of sediment concentration data to estimate the corresponding porewater concentrations will likely result in predictions much greater than "true" porewater levels (a metric of those compounds' availabilities.) We believe that including soot in our thinking will result in about a factor of 10 to 100 lower porewater levels, which implies that the sediment quality standards would be "too strict" by about that same factor.

Our finding that a significant quantity of "soot" is accumulating in coastal sediments may also have important implications to estimates of global carbon cycling. Since we would expect the soot carbon to be highly refractory, its burial is essentially a "permanent" removal of carbon in a "fixed form".

Finally, our flux results clearly reveal the high rates of vertical transport of hydrophobic organic chemicals on a per unit area basis for sites close to shore. However, it is the delivery of many metric tons of each chemical to the large expanses of the North Atlantic Ocean which accounts for the biggest terms in the global cycles of each compound.

## TRANSITIONS

The results of our work is clearly moving into the regulatory arena through the current reassessments of sediment quality criteria (which presumably the Navy will have to meet at their harbor facilities.) These findings affect evaluations of the need to cleanup contaminated sediments.

## RELATED PROJECTS

Our work has important ramifications for ONR-supported colleagues such as Dr. Larry Mayer, Dr. Lily Young, and Dr. Derek Lovely who are examining the roles of organisms (invertebrates and bacteria) in the cycling of organic pollutants like PAHs. We have recently initiated discussions with Dr. Mayer with regard to obtaining samples from pre-industrial core sections to explore further the relative importance of biomass versus fossil fuel burning as sources of the soot we find.

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